X.—*On the Isomeric forms of Valeric Acid.*

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IN the concluding pages of Frankland and Duppa's memoir on Synthetical researches on Ethers,* the authors state that ordinary valeric acid rotates a ray of polarized light to the right; whilst Wurtz had previously asserted that ordinary valeric acid is without any action upon a polarized ray. To reconcile these discrepant observations, Frankland and Duppa suggested that active amylic alcohol yields an active valeric acid when oxidized, and inactive amylic alcohol an inactive acid, and that the sample of amylic alcohol from which Wurtz's valeric acid had been prepared, was the inactive variety.

To test the validity of this suggestion, the two amylic alcohols were first separated by Pasteur's process, and then individually oxidized with a mixture of dipotassic dichromate and sulphuric acid in the usual manner. Equal weights of concentrated sulphuric acid and amylic alcohol were mixed together, the amylic alcohol being added very gradually; the mixture was then allowed to stand for 24 hours, and neutralized with baric carbonate, so as to form baric sulphamylate. The baric sulphamylate obtained from the active amylic alcohol, is, as stated by Pasteur, about two and a half times as soluble as that obtained from the inactive amylic alcohol; the mixed sulphamylates were consequently separated by fractional crystallisation, which was continued until the two salts were obtained in a state of purity.

Care must be taken to keep the solutions alkaline by baric hydrate, or the sulphamylates will decompose when heated. This process is long and tedious, as numerous crystallisations have to be made before the perfect separation of the sulphamylates is effected.

The two amylic alcohols were obtained by decomposing the baric sulphamylates with sodic carbonate, and again decomposing the sodic sulphamylates by ebullition with excess of

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sulphuric acid. The amylic alcohols thus obtained were purified by drying and rectification; they then exhibited the following characters:—

The amylic alcohol obtained from the less soluble sulphamylate, was found to boil at 129° C., and to have a penetrating and oppressive odour which produces coughing, and a burning taste. In the polariscope, when tested with a yellow sodium flame, it was found to be perfectly incapable of rotating the ray of polarized light.

The alcohol obtained from the soluble sulphamylate, had a boiling point of 128° C., and an odour resembling that of the inactive alcohol, but more fruity; it was, however, equally irritating, and had a burning taste. It was found to rotate a yellow ray of polarized light 17° to the left in a tube 50 centimetres long.

For the conversion of these alcohols into valeric acid, a hot oxidizing mixture was used, made by dissolving two parts of dipotassic dichromate in moderately hot water, and then adding three parts of concentrated sulphuric acid. The alcohol was added through a funnel tube slowly, the vessel containing the mixture being also connected with a condenser.

The inactive alcohol when oxidized was converted into valeric acid and amylic valerate, which latter was decomposed by sodic hydrate, and the resulting amylic alcohol again oxidized. There was no effervescence when the alcohol was added to the hot oxidizing mixture.

The active amylic alcohol when added to the nearly boiling oxidizing mixture, was found to effervesce strongly from the evolution of carbonic anhydride. On allowing the oxidizing mixture to cool, and then adding more of the alcohol, scarcely any effervescence was observed. It was allowed to stand for some hours, and then distilled, and the distillate was found to contain valeric acid and amylic valerate, which latter was again decomposed and oxidized as before.

The two valeric acids were freed from the accompanying water, which had distilled over with them, by neutralizing with pure sodic carbonate, evaporating to dryness, and decomposing with sulphuric acid. When dried and distilled, they had the following characters:

The valeric acid obtained from the inactive variety of amylic alcohol, boiled at 175° C., and had the characteristic persistent odour and taste of ordinary valeric acid. It was found when tested in the polariscope, not to possess the slightest action on the polarized ray. It is highly probable that this acid is identical with the isopropacetic acid $\left\{\begin{array}{l}\mathbf{C}\mathrm{Pr}\beta\mathrm{H}_2\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathbf{C}\mathrm{Me}_2\mathrm{H})\mathrm{H}_2\\ \mathbf{C}\mathrm{OHo}.\end{array}\right.$ obtained by Frankland and Duppa, and described in their memoir before mentioned. The boiling points of inactive valeric acid and of isopropacetic acid are identical.

The valeric acid from the rotating amylic alcohol boiled at about 170° C. and had the same disagreeable odour and taste as the inactive acid. When tested with the ray of polarized light, it gave a right-handed rotation of 43 degrees in a tube 50 centimetres long.

The above observations with the polariscope were most kindly taken by Dr. Frankland, to whom my most cordial thanks are due.

In order to ascertain the products of the graduated oxidation of the two amylic alcohols, some experiments were made by digesting them in sealed tubes at 100° C. with ordinary chromic acid oxidizing mixture.

When the rotating alcohol was thus treated, it evolved abundance of carbonic anhydride, and produced a large amount of acetic acid; while the inactive alcohol, which, when similarly digested, gave a mere trace of carbonic anhydride, seemed to produce scarcely anything but valeric acid.

The above experiments therefore indicate, either that the non-rotating valeric acid of Wurtz had been made, as suggested by Frankland and Duppa, from a non-rotating sample of amylic alcohol; or that the acid made from the mixed alcohols had been allowed to remain in contact with the hot oxidizing mixture sufficiently long to destroy the whole of the less stable rotating acid.

In a future paper I hope to be able to give a more detailed description of the oxidation products of the two alcohols, together with a comparison of the properties of the salts obtained from the two acids.